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On the Diffusion of a solute in Substitutional alloys

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Zh. tekhn. Fiz., 21(10), 1802-1811, 1954, U. S. S. R.

Summary A calculation is submitted of the diffusion coefficient of atoms which have penetrated into the internodes of body-centred cubic crystalline lattice of a binary alloy which may be in an ordered state.

Introduction

We shall consider the binary alloy of metals of the A and B substitutional type. Assume that the alloy has a body-centred cubic lattice and may be found in an ordered state. Assume that the atoms of any third element C have penetrated into the internodes of the crystalline lattice of the alloy A-B. It is assumed that the atoms C have a sufficiently small radius for it to be possible to neglect deviations of the lattice of the alloy A-B in the case of its penetration. The constant of the lattice a_0 and the energy of the interaction of different pairs of atoms will be considered to be independent of the composition of the alloy, of the concentration of the penetrating atoms, and of the degree of ordered arrangement.

The aim visualised is to determine the diffusion coefficient of the atoms C which have penetrated, assuming the presence in the alloy of a gradient of concentration of these atoms. It is well-known that current experimental methods make it possible to measure the diffusion coefficient at such temperatures that many alloys are in an ordered state. This affords the possibility in principle of studying by experiment the influence of ordered arrangement on diffusion, and enables the presentation of the calculation submitted below.

Section I. Determination of the mean height of potential barriers for the transition of penetrated atoms from one internode into an adjacent one.

It is well-known (1) that atoms C which have penetrated into internodes may assume positions of stable equilibrium corresponding to centres of the boundaries and to the mean of the edges of elementary cubic cells.

We shall call nodes of the crystalline lattice of an ordered alloy A-B determinative for atoms A, nodes of the first type, and nodes determinative for atom B, nodes of the second type. Assume for example that nodes of the first type are situated at the summits of cubic lattices and that nodes of the second type are at their centres. Then, among the internodes mentioned, there will be found internodes of the first type O_1 (centres of boundaries), having four adjacent nodes of the first type, at a distance $\frac{a_0}{\sqrt{2}}$ and two adjacent nodes of the second type at a distance (footnote 1) $\frac{a_0}{2}$ and internodes of the second type O_2 (centres of the edges), having four neighbouring nodes of the second type at an interval $\frac{a_0}{\sqrt{2}}$ and two neighbouring nodes of the first type at an interval of $\frac{a_0}{2}$. Consider now the positions

P of the penetrated atom C corresponding to the summit of the potential barrier for its transition from one internode into the nearest neighbouring internode, that is. from the centre of the boundary to the centre of the edge, or from the centre of the edge to the centre of the boundary. (We shall consider only these more probable transitions). It will be assumed that this position P is situated along the middle of the section joining

the said neighbouring internodes (footnote 2). Then, all positions P will have four nearest neighbouring nodes at a uniform interval $\frac{\sqrt{2}}{4} a_0$, among

which there will always be two nodes of the first type and two nodes of the second type. The nodes following in distance will be found to be a considerably greater distance $\frac{\sqrt{13}}{4} a_0$ from the distance P and these will be

neglected in the calculation of the potential energy of the atom C in the position P. We shall denote the energy of interaction of the pairs of CA and CB by v_{CA} and v_{CB} , putting

$$\left. \begin{aligned} v_{CA} \left(\frac{a_0}{\sqrt{2}} \right) &= -A, \quad v_{CA} \left(\frac{a_0}{2} \right) = -a, \quad v_{CA} \left(\frac{\sqrt{5}}{4} a_0 \right) = -\alpha \\ v_{CB} \left(\frac{a_0}{\sqrt{2}} \right) &= -B, \quad v_{CB} \left(\frac{a_0}{2} \right) = -b, \quad v_{CB} \left(\frac{\sqrt{5}}{4} a_0 \right) = -\beta \end{aligned} \right\} \quad (1)$$

We shall use the approximate method of calculation frequently applied in the theory of a solid body, which may be described as the method of mean energies. The essence of this method is that we shall not merely consider the difference of configuration of neighbouring atoms surrounding any atom of interest to us and leading to different values of the energy of its interaction with the nearest neighbours, but will assume that all atoms in position of a determined type (O_1 , O_2 and P) have a uniform energy of

interaction with neighbouring atoms, equal to the mean energy for all positions of the type considered. The use of this approximate method of course entails a certain degree of inaccuracy in the calculation. It may, however, be considered that the basic qualitative characteristic properties of the influence of order and composition on the diffusion coefficient will be the more correctly transmitted in such an approximate theory the less the difference between each other of the energies of interaction of the pairs CA and CB. Actually, calculations merely taking into account all possible configurations of atoms adjacent to that considered as taking part in the diffusion of atoms, and leading to considerably more cumbersome equations have shown that almost all basic qualitative characteristics of the solution are maintained also in this more precise theory. Above all, the evaluation of the error associated with the use of the method of mean energies was adopted for the constants selected further in section 4, when, in the interval of relative concentrations of the alloy A-B, differing from the value corresponding to the stoichiometric composition by no more than 0.20, the degree of error was found not to exceed 20% in terms giving the effect of order of the diffusion coefficient.

The probabilities of substitution for nuclei of the first and second type of atoms of A and B will be indicated respectively by

$P_A^{(1)}$, $P_A^{(2)}$, $P_B^{(1)}$, and $P_B^{(2)}$. Then, taking with the reverse sign the mean potential energy of the atom C from the position O_1 equals

$$U_{O_1} = 4 \left(P_A^{(1)} A + P_B^{(1)} B \right) + 2 \left(P_A^{(2)} a + P_B^{(2)} b \right). \quad (2)$$

In a quite similar manner, the potential energy of the atom C taken with the reverse sign in the position of the second type (O_2) may be written in the form:

$$U_{O_2} = 4 \left(P_A^{(2)} A + P_B^{(2)} B \right) + 2 \left(P_A^{(1)} a + P_B^{(1)} b \right) \quad (3)$$

and in the position P

$$U_P = 2 \left[(P_A^{(1)} + P_A^{(2)}) \alpha + (P_B^{(1)} + P_B^{(2)}) \beta \right] \quad (4)$$

We determine the mean height u_{12} of the potential barrier for the transition of the atom C from O_1 to O_2 (Figure 1). Clearly:

$$U_{12} = U_{O_1} - U_P = 4 (P_A^{(1)} A + P_B^{(1)} B) + 2(P_A^{(2)} \alpha + P_B^{(2)} b) - \\ - 2 \left[(P_A^{(1)} + P_A^{(2)}) \alpha + (P_B^{(1)} + P_B^{(2)}) \beta \right]. \quad (5)$$

For the transition from O_2 to O_1 the corresponding values will be equal to

$$U_{21} = U_{O_2} - U_P = 4 (P_A^{(2)} A + P_B^{(2)} B) + 2 (P_A^{(1)} a + P_B^{(1)} b) - \\ - 2 \left[(P_A^{(1)} + P_A^{(2)}) \alpha + (P_B^{(1)} + P_B^{(2)}) \beta \right] \quad (6)$$

The positive character of the values of u_{12} and u_{21} should be considered as limitations imposed on the possible selection of parameters A, B, a, b, α and β .

Section 2. Distribution of included atoms C along internodes of the first and second type.

We shall denote by n the concentration of included atoms (number of atoms of C in 1 cm^3). These atoms have different energy in the internodes O_1 and O_2 . By n_1 and n_2 respectively we denote the concentrations of the atoms C in the internodes O_1 and O_2 . Then:

$$\frac{n_1}{n_2} = e^{\frac{U_{O_1} - U_{O_2}}{kT}} \quad (7)$$

Utilising the fact that $n_1 + n_2 = n$ and introducing the designation

$$\Delta U = U_{O_1} - U_{O_2} = U_{12} - U_{21} \quad (8)$$

we obtain the following expressions for n_1 and n_2 :

$$n_1 = n \frac{1}{1 + e^{-\frac{\Delta v}{kT}}}, \quad (9)$$

$$n_2 = n \frac{1}{1 + e^{\frac{\Delta v}{kT}}}$$

This same result may be obtained by another method considering transitions of atoms C from the position O_1 to O_2 (in the case of grad $n = 0$), and also from the position O_2 to O_1 and equating the number of transitions of both types, completed in unit time, that is from the equilibrium condition (20).

Section 3. Determination of the diffusion coefficient of included atoms

Assume in the alloy the creation of a gradient of concentration of atoms C along the x axis parallel to the edge of the cubic nucleus. Consider two neighbouring atomic planes in the alloy A-B, perpendicular to the x-axis, which will be denoted I and II (Figure 2). The distance between these planes $dx = \frac{a_0}{2}$. On these same planes are situated also the atoms C,

which are in the internodes. Assume that the plane I passes through nodes of the second type. For one square centimetre of this plane, there will be $\frac{2}{3} \frac{1}{a_0^2}$ of the internode type O_1 and $\frac{1}{3} \frac{1}{a_0^2}$ of the type O_2 . Further, for 1 cm² of the plane II, which passes through nodes of the first type there are situated $\frac{1}{3} \frac{1}{a_0^2}$ positions of the type O_1 and $\frac{2}{3} \frac{1}{a_0^2}$ positions of the type O_2 . It is easy to find that the probabilities of substitution of an internode of the type O_1 and O_2 by the atom C are equal respectively to

$$W_1 = \frac{1}{3} n_1 a_0^3 \text{ and } W_2 = \frac{1}{3} n_2 a_0^3. \quad (10)$$

Therefore, on 1 cm² of the plane I (intersecting the x axis at the point x), will be located

$$v_{O_1}^I = \frac{2}{3} a_0 n_1 (x) \quad (11)$$

of atoms C in the internodes of type O_1 and

$$v_{O_2}^I = \frac{1}{3} a_0 n_2 (x) \quad (12)$$

of atoms C in internodes of the type O_2 .

On one cm² of the plane II (intersecting the x-axis at the point $x + dx$) we find

$$v_{O_1}^{II} = \frac{1}{3} a_0 n_1 (x + dx) \quad (13)$$

of atoms C in internodes of the type O_1 and

$$v_{O_2}^{II} = \frac{2}{3} a_0 n_2 (x + dx) \quad (14)$$

of atoms C in internodes of the type O_2 .

We determine the number of atoms C which pass per second from 1 cm² of the plane I onto the plane II. It will be seen from Figure 2 that the transitions shown can be achieved only by atoms C located on the plane I, in internodes of the type O₁, when they will pass into internodes of the type O₂ (on the plane II). We shall henceforward restrict consideration to the particular case when the concentration n of atoms C is small by comparison with a number of internodes per 1 cm³. Then, it is possible to neglect such rare events as the presence of two atoms in neighbouring internodes, one of which is situated on the plane I, and the other on the plane II.

In this connection the probability of transition of one atom C from the plane I from an internode of the type O₁ onto a determined internode of the type O₂ of the plane II, per unit time, as is known (2), may be written in the following form:

$$W_{12} = \frac{1}{\tau} e^{-\frac{u_{12}}{kT}} \quad (15)$$

The value τ will be considered to be approximately independent of the composition and order in the alloy. The atom C considered on the plane I may pass only into one neighbouring internode on the plane II. The number of atoms C therefore, passing per unit time from 1 cm² of the plane I onto the plane II, equals

$$S_{I \rightarrow II} = \nu_{O_1} W_{12} = \frac{2}{3} \frac{a_0}{\tau} n_1(x) e^{-\frac{u_{12}}{kT}} \quad (16)$$

We calculate the flow $S_{II \rightarrow I}$ of atoms C. In the precisely similar way, we obtain

$$S_{II \rightarrow I} = \nu_{O_2}^{II} W_{21},$$

where the probability of transition of the atom C from an internode of type O₂ onto a determined neighbouring internode of type O₁ has the form:

$$W_{21} = \frac{1}{\tau} e^{-\frac{u_{21}}{kT}} \quad (17)$$

$$\text{Thus, } S_{II \rightarrow I} = \frac{2}{3} \frac{a_0}{\tau} n_2(x + dx) e^{-\frac{u_{21}}{kT}} \quad (18)$$

$$\text{Noting that } n_2(x + dx) \approx n_2(x) + \frac{dn_2(x)}{dx} dx,$$

where $dx = \frac{a_0}{2}$ we obtain for the resulting diffusion flow S of atom C the following expression:

$$S = S_{I \rightarrow II} - S_{II \rightarrow I} = \frac{2}{3} \frac{a_0}{\tau} \left[n_1(x) e^{-\frac{u_{12}}{kT}} - n_2(x) e^{-\frac{u_{21}}{kT}} - \frac{dn_2}{dx} \frac{a_0}{2} e^{-\frac{u_{21}}{kT}} \right] \quad (19)$$

The first two components in square brackets of equation (19) refer to one and the same value of x . It is therefore possible to consider them for the case when $\text{grad } n = 0$, and consequently $\frac{dn_2}{dx} = 0$. In the meantime, the

diffusion flow S must be equated to zero, which, according to (19) takes place if the following equilibrium condition is fulfilled

$$n_1(x) e^{-\frac{u_{12}}{kT}} = n_2(x) e^{-\frac{u_{21}}{kT}} \quad (20)$$

It is easy to see that this equation is actually satisfied by the expressions found above, (9) for n_1 and n_2 . Thus, applying (20) and (9), from (19) we get:

$$S = -D \frac{dn}{dx} \quad (21)$$

Here, the diffusion coefficient D of atoms C has the form

$$D = \frac{a_0^2}{3\tau} e^{-\frac{u_{12}}{kT}} \frac{1}{1 + e^{-\frac{\Delta u}{kT}}} \quad (22)$$

which, utilising (8) can be written in the form:

$$D = \frac{a_0^2}{3\tau} e^{-\frac{u_{12}}{kT}} \frac{1}{1 + e^{-\frac{\Delta u}{kT}}} \quad (23)$$

or in the symmetrical form

$$D = \frac{a_0^2}{3\tau} \frac{1}{e^{\frac{u_{12}}{kT}} + e^{\frac{u_{21}}{kT}}} \quad (24)$$

The dependence of the values u_{12} , u_{21} and ΔU on the relative concentration c of the atom A in the alloy A-B, and on the degree of further order

(1)
 $\eta = \frac{P_A - C}{q - C}$ (where $q = 2c$ for $c < \frac{1}{2}$ and $q = 1$ for $c > \frac{1}{2}$) may be found with the aid of the known equations (footnote 3) for the probability of substitution of nodes of the lattice

$$\left. \begin{aligned} P_A^{(1)} &= C + \gamma \eta, & P_B^{(1)} &= 1 - C - \gamma \eta, \\ P_A^{(2)} &= C - \gamma \eta, & P_B^{(2)} &= 1 - C + \gamma \eta, \end{aligned} \right\} \quad (25)$$

where $\gamma = q - c$.

Applying (8) (6) and (25) we find

$$\Delta U = 2u'', \quad u_{12} = u' + u'', \quad u_{21} = u' - u'',$$

$$\begin{aligned} \text{where } u' &= 2 \{ 2 [C_A + (1 - C) B] + C_A + (1 - C) b - 2 [C_A + (1 - C) \beta] \}, \\ u'' &= 2 [2 (A - B) - a + b] \gamma \eta. \end{aligned} \quad (26)$$

Then

$$D = D_0 e^{-\frac{u^*}{kT}} \frac{1}{\frac{u''}{ch kT}} \quad (27)$$

$$\text{where } D_0 = \frac{a_0^2}{b\tau}$$

Equations (26) and (27) give the relationship between the diffusion coefficient D of the included atoms and the composition and degree of further order of the alloy A-B. In the determination of the temperature and concentration relationship of D in the ordered state of the alloy, it is necessary to consider that on the temperature and composition depends also the degree of further order η . To evaluate the character of this relationship, it is possible to use the equation of order familiar from statistical theory

$$\frac{16\gamma\epsilon}{kT} \eta = \log \frac{(1 - C + \gamma\eta)(C + \gamma\eta)}{(1 - C - \gamma\eta)(C - \gamma\eta)}, \quad (28)$$

where ϵ is the characteristic constant for the given ordered alloy, associated with energies of interaction v of pairs of neighbouring atoms in the alloy A-B by the equation

$$\epsilon = 2 V_{AB} \left(\frac{\sqrt{3}}{2} a_0 \right) - V_{AA} \left(\frac{\sqrt{3}}{2} a_0 \right) - V_{BB} \left(\frac{\sqrt{3}}{2} a_0 \right) \quad (29)$$

and with the temperature T_0 of the transition order-disorder by the relationship

$$T_0 = \frac{8\epsilon}{k} c (1 - c). \quad (30)$$

From (28) it is possible in the case of every value of c to find graphically the dependence of $\eta(T)$.

Section 4. Assessment of results.

Analysis of the equations obtained leads to the following conclusions.

1. Temperature relationship of the diffusion coefficient

From (27) it follows that for $T > T_0$, when $\eta = 0$, and $\frac{u''}{kT} = 1$, the curve for the dependence of $\log D$ on $\frac{1}{T}$ represents a straight line. The same type of dependence is obtained in the case of unordered alloys A-B for arbitrary temperatures. For ordered alloys, at the point $T = T_0$ the curve examined has a break and at $T < T_0$ (when $\eta \neq 0$) it does not appear as a straight line. However, at sufficiently low temperatures the relationship between $\log D$ and $\frac{1}{T}$ again differs little from the linear. On figure 3 are shown curves illustrating the temperature relationship of $\log D$ for different compositions (footnote 4) obtained in accordance with (27) and (28). In this connection, the constants entering into the equation were selected in the following manner: $2i = 0.255$ eV, $2B = 0.36$ eV, $2a = 0.36$ eV, $2b = 0.375$ eV, $2a = 0.375$ eV, $2B = 0.45$ eV and $\epsilon = 0.0352$ eV.

It will be noted that divergences from the rectilinear relationship between $\log D$ and $\frac{1}{T}$ may in accordance with (27) be anticipated also in these cases when atoms of the third included element C diffuse in the crystalline lattice of any binary compound, the atoms of which at all temperatures up to the melting point retain complete order. In this case,

however, the divergence from the rectilinear will be obtained only on account of the presence of a multiplier $(\exp \frac{u''}{kT})^{-1}$ not equal to unity in equation (27), and not on account of a change in the degree of further order with temperature.

The divergence indicated, therefore, will be expressed not so markedly as in the case considered earlier. It should be stressed that in ordered alloys it is not possible to characterise the alloy by a constant not depending on the temperature of the energies of activation, for diffusion of atoms C.

2. Concentration dependence of the diffusion coefficient

In the unordered state of the alloy, (in the unordered alloys or in the ordered for $T > T_0$)

$$D = D_0 e^{-\frac{u'}{kT}}$$

where u' is a linear function of the concentration c of atoms A in the alloy A-B and the dependence of D on c for $T = \text{const}$ has a smooth character without the presence of any sharp extremes near the value $c = 0.5$ corresponding to the stoichiometric relationship (see top curve on Figure 4). In the ordered state of the alloy A-B, the curves of the dependence $D(c)$ in the case of constant values of T acquire a tendency to have minima at values of c in the vicinity of $c = 0.5$.

Curves of this type constructed in accordance with (27) and (28) in the case of the values given above for the constants are shown on Figure 4. The broken curve on this figure joins points of the curves with abscissae equal to the composition of the alloys, for which the temperatures corresponding to the curve $\frac{D(c)}{D_0}$ are critical temperatures T_0 . The top curve

(for $T = 850^\circ\text{K}$) gives the relationship $D(c)$ for alloys among which already the alloy of stoichiometric composition is unordered.

It will be seen therefore, that in ordered alloys we should expect characteristic peculiarities of temperature and concentration dependence of the coefficient of diffusion which do not take place in pure metals and in unordered alloys.

It may again be noted that for autodiffusion also, in ordered alloys, proceeding by way of substitution of gaps on the nodes of the crystalline lattice similar characteristics should be expected. This is indicated by calculations (4 and 5) of the equilibrium number of gaps on the nodes of both types in crystalline lattices. In this connection, as was shown in (5) for the face centred cubic lattice we should expect a spasmodic change of the diffusion coefficient with the temperature at $T = T_0$.

In connection with what has been stated above, it would be interesting to perform experimental investigations on diffusion in ordered alloys to disclose by experiment the characteristics indicated.

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FOOTNOTES

1. Consideration of only two near neighbours would here give too coarse results. Therefore, for internodes we shall consider also the presence of the following four nodes in extent.
2. This simplifying assumption does not entail appreciable errors, since we are considering the alloys A-B representing solid solutions of the substitution type with fairly extensive solubility, formed from atoms A and B with near atomic radii and single type force fields.
3. See for example Bibl. 3) equations 31) for $\nu = \frac{1}{2}$.
4. Here and subsequently the curves were constructed by A. A. Krivoglas.
5. Journal of Technical Physics, Vol. 24, No. 10.

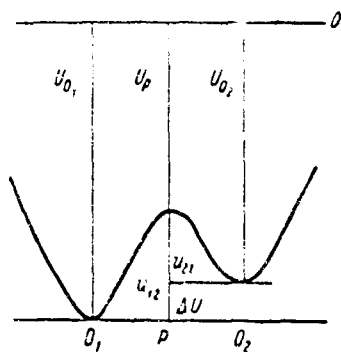


Рис. 1.

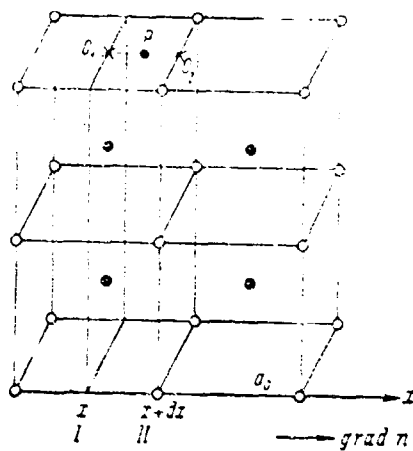


Рис. 2.

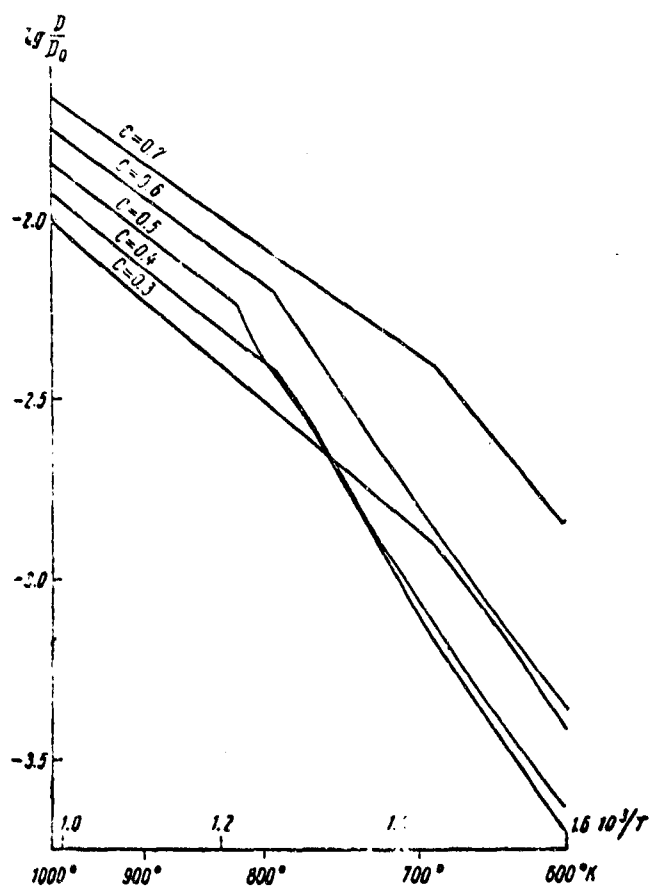


Рис. 3.

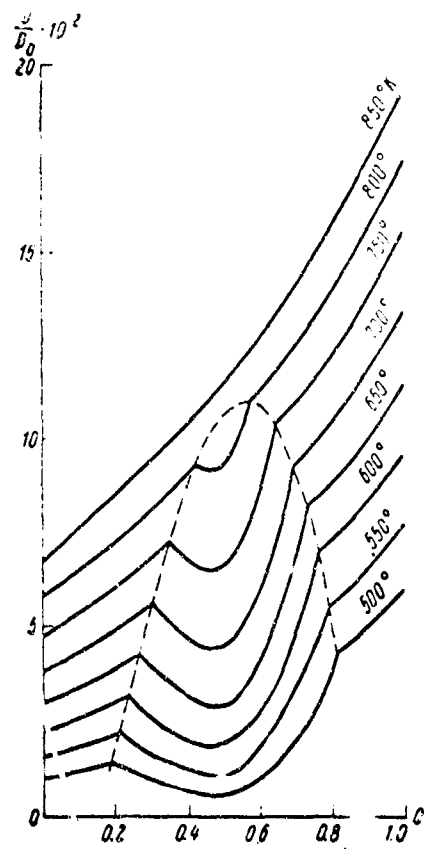


Рис. 4.